

SELECTIVE CO METHANATION CATALYSIS

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INTRODUCTION

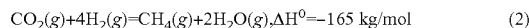
In recent years, fuel processing including hydrogen generation, purification, and storage is drawing a great deal of attention. Fuel cell systems are being developed for several applications, including distributed and portable power generation and for consumer applications¹. At Pacific Northwest National Laboratory (PNNL) much development has been done in the area of fuel processing for portable power generation using microchannel technology^{2,3,4}. Typical fuel processing strategies include steam reforming, partial oxidation and—as a combination of these processes—autothermal reforming⁵. Both preferential oxidation and autothermal reforming introduce oxygen (air) into the system and burn with the reforming fuel to produce the heat required for the reforming reactions(s) to occur. In steam reforming, an external combustor is used to provide the heat. While each technology has advantages and disadvantages, steam reforming is usually used because it offers the highest theoretical efficiency, and produces the highest hydrogen composition³. All three reforming strategies, however, may require additional removal of carbon monoxide since the current permeable membrane fuel cell (PEMFC) cannot operate with carbon monoxide levels higher than several ppm.

After reforming of hydrocarbons or higher alcohols and water-gas-shift the CO concentration in the reformer gas is usually reduced to 1-2%⁶. Reforming of methanol can directly yield a CO concentration in the same range with no need for a water-gas-shift step². Either way, further “deep removal” of CO to concentrations below 100 ppm for even the most tolerant fuel cell electrode catalysts is needed.

Three processes have been suggested to reduce CO in the feed; preferential, or selective oxidation, methanation, and membrane separation⁷. Preferential oxidation catalytically oxidizes CO to CO₂. Disadvantages include undesirable H₂ oxidation and the complexity of having to add precisely controlled amounts of oxygen (air) to the system⁶. Nonetheless, much focus in the literature has been on developing preferential oxidation catalysts and it considered by many to be the primary choice for the removal of CO from hydrogen-rich streams⁹. Hydrogen permeable membranes, usually employing Pd-based membranes, separate hydrogen from the other components (i.e. CO, CO₂, H₂O). This purification system can be beneficial where pure H₂ is desired. The main problems with palladium membranes are that they require a high pressure differential, which takes a toll on overall systems efficiency, they usually require temperatures in excess of 350° C., have a high cost associated with the need for a great amount of noble metal, and membrane lifetime is an issue⁶. Finally, removal of CO by means of methanation has long been known as a possible strategy^{6,7,9}.

CO methanation by reacting it with hydrogen is shown in Eq (1). The methane produced will act as an inert diluent and will thus not react in the fuel cell. A disadvantage is the hydrogen penalty. It can be seen from Eq (1) that for every mole of CO, three moles of H₂ are also reacted. Furthermore, the undesirable reaction of CO₂ methanation is shown in Eq

(2). For every mole of CO₂, four moles of H₂ are reacted⁶. A second undesirable reaction is the reverse-water-gas-shift (RWGS) reaction, shown in Eq (3). CO₂, which there is usually 10 to 20 times more of than CO, can shift to CO. In order to minimize Eq (3) the temperature must be kept as low as possible to minimize shift activity as much as possible.



Methanation has the benefit of being a somewhat simple, passive process, since it does not require any oxygen (air) addition, and it is only necessary to control the temperature¹⁰. However, the high hydrogen consumption required for both the CO methanation and undesirable CO₂ methanation painfully cuts into fuel efficiency. Thus, many do not believe methanation is feasible at CO concentrations in the percent range^{6,7}. Some have proposed using methanation downstream from other CO removal processes, such as preferential CO oxidation, to cleanup any remaining amounts of CO (usually <0.1%).

Baker et al. reported using a ruthenium or rhodium on an alumina support catalyst to selectively hydrogenate carbon monoxide containing high concentrations of carbon dioxide. However, the CO feed concentration used of 0.29% was considerably lower than the percent range needed for current applications as a stand alone process. Additionally, relatively low feed flowrates from GHSV=500-2000 hr⁻¹ were reported. Microreactors at PNNL typically operate at much higher throughputs from 10,000-60,000 hr⁻¹ to maximize reactor efficiency. Even with these lower flowrates the operating temperature ranges where the CO remained below 100 ppm, are undesirably small. Also, only temperatures up to 220° C. were reported. It was found that for a given feed gas, the critical temperature range is shifted somewhat higher as the feed gas average space velocity is increased and also as the feed gas water vapor content is increased.

Rehmat et. al. investigated this process at much higher space velocities of 9000-36,000 hr⁻¹ and higher temperatures of 125° C.-300° C.¹². A similar feed as that of Baker et. al. was used (3000 ppm CO). The higher space velocity tests did not yield CO outputs lower than 100 ppm. They reported nickel catalysts as being active but that ruthenium was the most effective CO selective methanation catalyst tested. Furthermore, they showed that in the absence of CO₂ the methanation reaction goes to almost completion at temperatures higher than that necessary to achieve the minimal CO output, when CO₂ is added (under similar space velocities). Thus, it was suggested that while it is possible that for all the temperatures investigated the CO methanation reaction Eq (1) takes place along with the reverse shift reaction Eq (3), the latter is less noticeable up to an optimal temperature. After reaching this temperature where the CO is lowest, the reverse shift reaction begins. Bohm et. al. described a process utilizing in part selective methanation using a Ru— and TiO₂— containing catalyst¹³. Van Keulen patented a two-stage, two-temperature range methanation process which utilized a Ru-based catalyst¹⁴. In a recent work by Otsuka et. al., several supports and metals were studied for CO methanation¹⁵. The most promising catalysts—Ni/ZrO₂ and Ru/TiO₂ catalysts—were studied in the presence of CO₂. It was found that while these catalysts can catalyze the methanation of CO selectively in the presence of CO₂ the temperature ranges effective are narrow for both catalysts. For example, for the operating conditions reported, the methane output increased 4-fold in